

Portable device for the detection of nitro-explosives based on optical properties of sensor's material

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Abstract. The aim of this study was to design a device for explosives detection. The study design is based on excited steady-state luminescence quenching registration. Sensor's material luminescence intensity reduction occurs due to an interaction of explosives vapours contained in the air. The decrease rate of the luminescence intensity indicates the concentration of vapours. To study the luminescent properties of the sensor element, its luminescence spectra excited by photons with energies in the range 280 - 425 nm were measured. The excitation photoluminescence spectra for luminescence bands of the sensor element were also measured. Excitation source was light emitting diode (375 nm) and luminescent signal receiver was a photodiode (430 - 650 nm) in device designed. The device is operated under control of a program. The algorithm provides multiple operating modes (configuration, calibration, measurement etc.). Thus this device is referred to the class of devices with increased sensitivity to the explosives vapors. The advantages of device are autonomic power, small weight and sizes, simplicity of device operation for measurements.

1. Introduction

The luminescent properties of various compounds are widely utilized in chemical, biological, and medical engineering due to high sensitivity and unique opportunities to study molecules' excited states, photochemical reactions, dynamics of fast molecular processes, as well as structure and properties of complex chemical and biological objects.

Fluorescence quenching is a process that reduces the induced light flow intensity. Several processes can lead to this phenomenon, including reactions in excited state, energy transport, the formation of complexes at quencher molecules collisions with fluorescent substance molecules (molecules-sensors). Prerequisite of this effect demonstration is contact between them. Currently, fluorescence quenching is used in various practical applications, including explosives detection. The development of new devices that are capable detecting traces of explosive materials (HE) may help to eradicate terrorism

Therefore, the goal of this study was to evaluate luminescent characteristics of sensor materials to describe parameters that may be considered during a development process of a mobile device for detection of explosive materials traces.



2. Experimental part

A method for the synthesis of new monomolecular fluorescent compounds that consist of poly-aromatic heterocyclic systems with flat and branched architecture fragments was utilized in this study. The details of this technology are described [2-4]. Chemical compounds that were obtained as a result of the utilization of the above described technology are sensitive to vapours of trinitrotoluene (TNT) and its derivatives as well as to hard-detected nitro HE-like hexogen.

Powder of polyaromatic π -conjugated system was dissolved in an organic solvent. The obtained colloidal solution was electrospun with the help of viscose matrix. Thereafter the obtained samples were dried and used in the experimental procedure. Photoluminescence (PL) and PL excitation spectra of studied material, containing the molecules-sensors are presented in Figure 1 и 2.

It can be seen that the full range of luminescence is in the limit of 400 - 650 nm, the efficient luminescence of the material is observed in the range of 425 - 550 nm, and the most intensive luminescence bands are with maximum range of 447 to 474 nm.

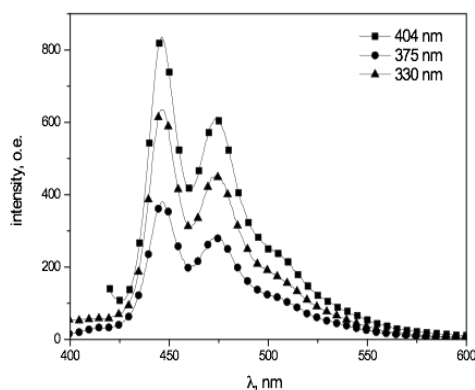


Figure 1. PL spectra of material at excitation by photons in wavelength range of 330-404nm. Luminescence excitation wavelengths are indicated in figure legend.

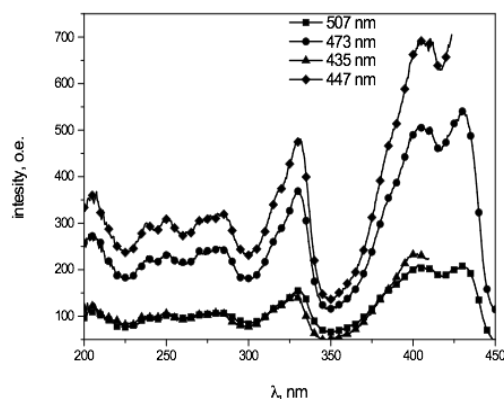


Figure 2. Excitation spectra of the main luminescence bands of sensor.

There were observed luminescence bands with maxima at 447, 473 and 507 nm under excitation by photons with energy of 330 nm and 375-450 nm.

3. Theoretical part

The nitroaromatic compounds luminescence detection method is based on the change of fluorescence quantum yield or excited state lifetime of the donor molecule of sensor due to the total or partial electron transport in contact with nitroaromatic compounds.

During interaction with fluorescent molecule-sensor (chemosensor) the analyzed molecule reduces the intensity of light. This phenomenon is obeyed by the law, known as Stern-Volmer equation, which is a mathematical description of fluorescence quenching phenomenon [5]:

$$\frac{I_0}{I} = (1 + K_A [Q])(1 + k_q \tau_0 [Q]),$$

where:

I_0 - luminescence intensity in the absence of analyzed substance;

I - luminescence intensity in the presence of analyzed substance;

$[Q]$ - substance concentration (I depends on it);

KA - binding constant - represents the contribution of so-called static quenching, which occurs through the formation of donor-acceptor complex between the sensor in the ground state and nitroaromatic compound;

τ_0 - lifetime of the excited state of the molecule-sensor photoluminescence at photoexcitation for dynamic quenching process;

kq - interaction rate between the molecule of analyzed substance and molecule-indicator.

In most cases, the quenching constants for Stern-Volmer I0/I are determined by the contribution of prevailing in a particular case type of quenching.

In the case of both static and dynamic quenching the fluorescence decrease is due to electron transport from the molecule-sensor in the ground or excited state to molecule of nitroaromatic compound in the ground state.

A simplified diagram of the fluorescence quenching by nitro compounds is shown in Figure 3.

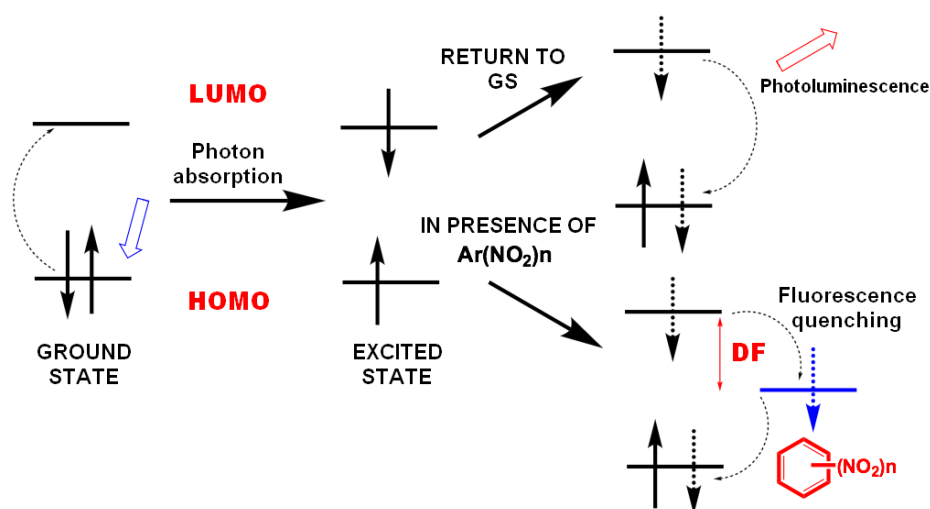


Figure 3. The mechanism of fluorescence quenching by contact of chemical sensor and nitro compounds. LUMO - the lowest unoccupied molecular orbital, the HOMO - the highest occupied molecular orbital, DF - driving force. The arrows indicate the radiative and non-radiative transitions of electrons.

At photoexcitation of molecule-sensor the electron makes a transition to the molecular orbital of higher energy. In the absence of quencher, the reverse transition is accompanied by photoluminescence. Upon contact with the nitro compound the excited electron of molecule-sensor returns to the ground state not participating in the radiative transition, which is observed experimentally as fluorescence quenching. The energy difference between HOMO and LUMO is driving force (DF) of fluorescence quenching process (Figure 3).

In most cases, the static fluorescence quenching is prevalent and therefore it is often used in nitroaromatic compounds luminescent detection. The quenching presence of static nature primarily is judged by high values (10^3 M^{-1} or higher) of complexation constants (quenching constants) between nitroaromatic compounds and molecules of photoluminescent sensors (typically electron-rich (hetero) aromatic compounds). The lifetime of excited state of photoluminescence chemosensors with increasing concentration of nitroaromatic compounds remains unchanged.

4. Practical part

During development of device for explosives traces detection the experimental results and the estimated model of quenching process shown in Figure 3 are taken into account. It is necessary to use

photons with energy at 330 nm, or in the integral mode in the wavelength range of 375-450 nm to obtain maximum sensitivity of material to HE and to excite the efficient luminescence.

Based on the fluorescent material characteristics, a device that meets the following requirements has been designed: air pumping with constant rate through the sensor element comprising luminescent material (chemosensors);

- impact of light source with wavelength corresponding to excitation of luminescence on the surface and in the surface layer of sensor element;
- luminescence intensity measurement by photosensitive element; it concludes vapor concentration of nitro HE on the dynamics of concentration change in time.

As the source of luminescence excitation in device there were selected a light emitting diode with indicated energy range and luminescent signal photodetector - photodiode with sensitivity in the range of 430 - 1100 nm. To prevent exciting photons to photodetector, it was placed in front of photodetector the cutting optical filter with transmission wavelength above 425 nm.

Table 1. The device has the following characteristics.

Characteristics	Value
measurement range of luminous flux:	0.0015 - 0.1 lm;
measurement error of luminous flux:	not less than 0.1 %;
luminescence excitation wavelength:	375 nm;
luminescence detection range:	from 430 to 650 nm.

Block diagram of device is shown in Figure 4.

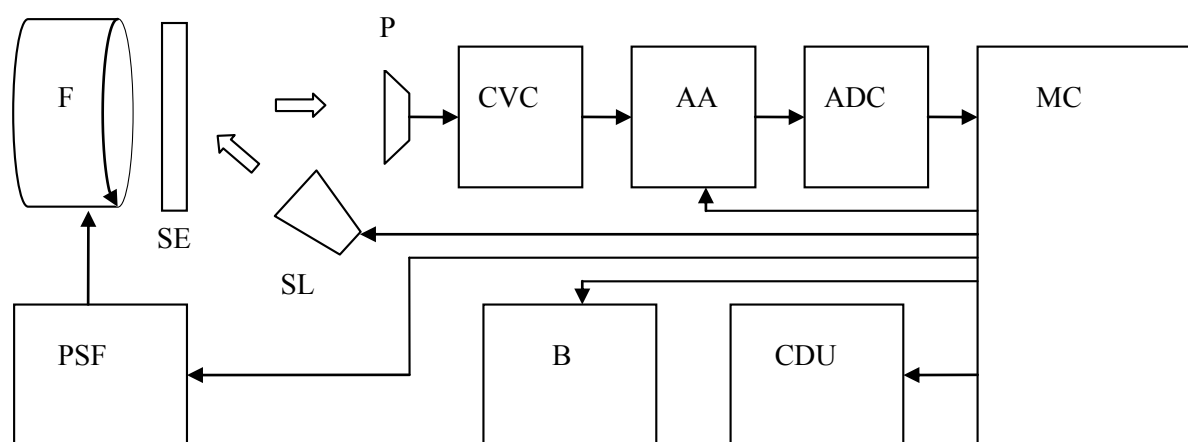


Figure 4. Block diagram of device for explosives and narcotics detection.

The device comprises the following basic structural units: fan (F); sensor element (SE); source of exciting the luminescence light (SL); photocell for luminescence intensity registration (P); current-to-voltage convertor (CVC); amplifier with adjustable amplification factor (AA); analog-to-digital converter (ADC); microcontroller (MC); buzzer (B); control and display unit (CDU); fan power supply (PS).

CVC converts a current of P that is proportional to the intensity of light into a signal of voltage that is the most suitable for further converting. AA is used for further signal amplification and to bring it to the range of optimal value of electric signal applied to ADC.

The device functioning is controlled by microcontroller unit. Device switching on and off, mode selection, display and reading information is produced by CDU. Multilevel menu is displayed on

device indicator. The upper level corresponds to device selection mode, the bottom level - to mode value. All information about measurement time, results and their status (test, search, fighting etc.) is stored in non-volatile memory of device. You can connect device to PC via USB interface, built-in MC. In this mode, it is transferred the device control to PC and provided access to device database. B is sound alarm to detect HE and serves as main indicator of this event. B can be either built-in or plug-in to the standard connector.

PS provides a constant fan speed in case of significant supply voltage change during battery discharge in operation process. The device is powered by rechargeable battery. Its charge is made from specialized charger.

5. Conclusion

Experimental results and estimated model of sensor photoluminescence quenching processes allowed us to develop and make the layout version of device for explosive vapors detection. The testing with HE-DNT simulator and real devices will be carried out.

6. References

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